

Study of Electrode Surface by IR Spectroscopy

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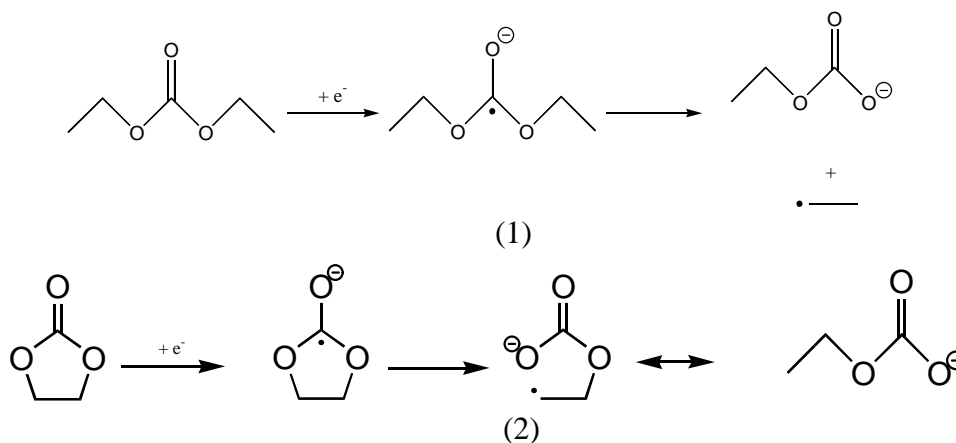
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BACKGROUND

Advance Technology Development (ATD) Program is a new program put forth by Department of Energy to develop high power lithium ion batteries for hybrid electric vehicles and electric vehicles. It is a joint effort of five national labs and LBNL is the lead lab in investigating SEI (solid electrolyte interface) layer formation and dissolution. Our group is responsible for the characterization of SEI utilizing Infrared Spectroscopy.

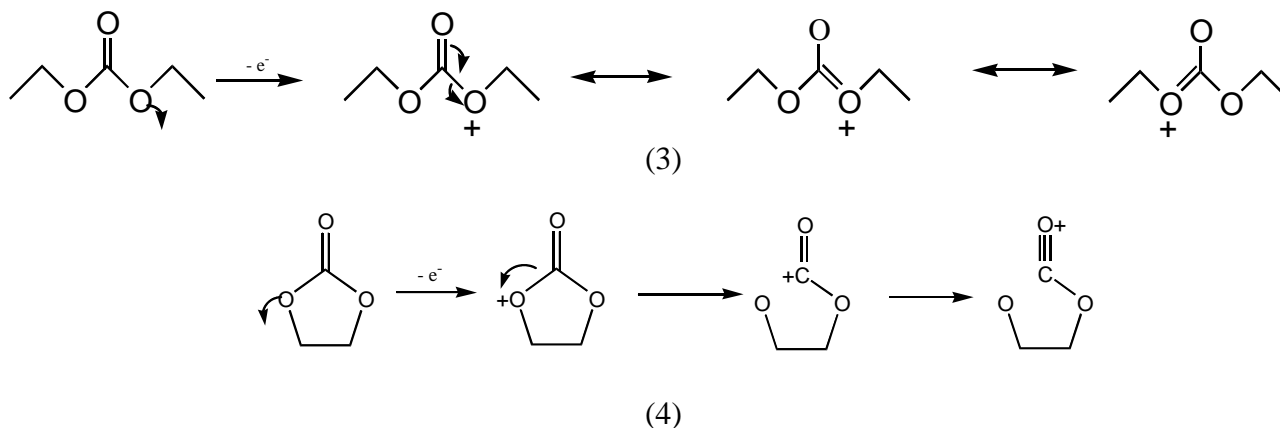
The basic electrochemistry of lithium ion battery involves only the transfer of Li^+ ions between the two insertion electrodes (anode and cathode), therefore it is also called the rocking chair battery. The electrolyte commonly employed in lithium ion batteries is mixture of aprotic organic solvents and lithium salt such as LiPF_6 . The cells operate in a wide electrochemical potential window (0 to 5 volts versus Li/Li^+) which is beyond the thermodynamic limit of the organic electrolyte and therefore, the electrolyte is being reduced and oxidized at the anode and cathode respectively during the charging process. Fortunately, the decomposition product forms a protective film (SEI layer) on the electrode surface, which is electronic insulating but ionic conducting. It allows the transportation of the Li^+ ions, but prevent further decomposition of the electrolyte. Therefore, SEI formation is crucial in the operation of lithium and lithium ion batteries, dissolution of which is believed to closely relate to the battery failure.

Density functional theory and Ab initio calculations were performed by our group recently [1] to look at the reduction and oxidation mechanisms of common organic solvent used in lithium and lithium ion batteries, including diethyl carbonate (DEC (1)) and ethylene carbonate (EC (2)) which are currently employed in the ATD cells. Their reduction mechanisms are proposed below:



The reduction products are lithium alkyl carbonate (LiOCO_2R). This agrees well with findings from many other investigators [2, 3] and infrared spectroscopy is commonly employed as a characterization tool. The stretching of $\text{C}=\text{O}$ in LiOCO_2R is intense and characteristic, which shifts to lower frequency (~ 1650) from $\sim 1800\text{ cm}^{-1}$ for the carbonate molecules. In comparison of the large amount of investigations on solvent reduction, few studies are done on their oxidation mechanisms. Scheme 3 and 4 are oxidation mechanisms proposed in recent theoretical study performed by our group.

Radical cations are the reaction intermediates in solvent oxidation, which could possibly lead to cationic polymerization of the solvent molecules on the cathode surface.



PRESENT ACCOMPLISHMENTS

The electrode samples are harvested from real batteries. They are heterogeneous and contain electrode active material, carbon black, binders and etc. The SEI layer is, therefore, only formed on the active materials. The small spot size ($1 \sim 7 \mu\text{m}$) of the synchrotron beam provides not only the necessary spatial resolution but also a much higher signal to noise ratio. The SEI layers on both electrodes were observed to be extremely air sensitive. For example, LiOCO_2R could react with H_2O and CO_2 in air to form Li_2CO_3 . Airtight IR microscope cells with KBr windows were constructed with the help from Dr. Michael Martin to perform IR microscopy on air-sensitive and moisture-sensitive electrode materials. Electrode samples were inserted into the IR cells in a dry box. The method allows one to look at SEI formed on the electrode surface without excessive handling, and avoids introduction of other impurities.

During 1999, we have performed IR measurements on five ATD cells utilizing synchrotron beam in ALS. Four of these cells are unused cells that have only been through two formation cycles and one discharge. Chemistry of these cells is most simplified and may serve as the basis of our understanding of cells cycled at different conditions. IR data shows that SEI layer (mostly LiOCO_2R) is formed on the anode during the formation cycles, as shown in Figure 2 for anode 132. For cell 117 that was cycled many times at 70°C and failed, a more

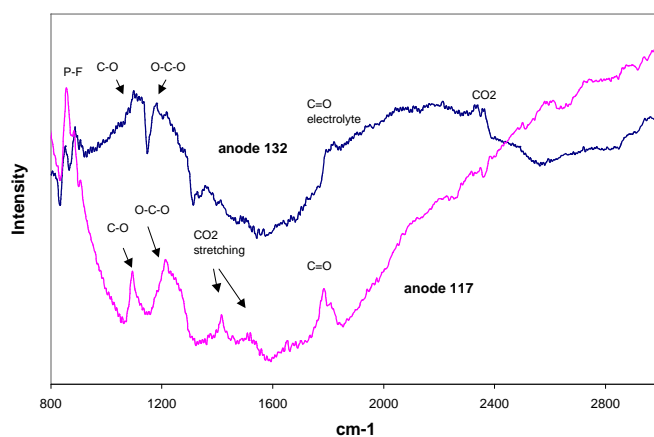


Figure 2 SEI layer observed on anode

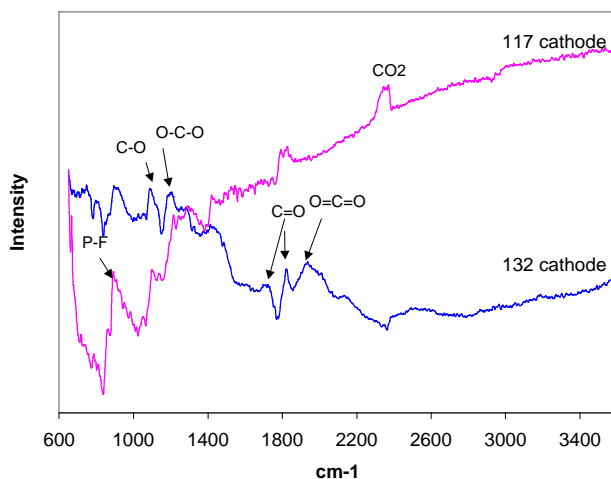


Figure 3 IR data of cathode

homogeneous SEI layer was observed (Figure 2). The strong O-C-O stretching at 1280 cm^{-1} indicates that anionic polymerization of EC may have occurred, results in a $(-\text{C}_2\text{H}_4\text{OCO}_2\text{C}_2\text{H}_4\text{O}-)_n$ moiety. [4]

On the cathode, solvents were oxidized and similar SEI layers were observed for both unused cell 132 and cycled cell 117, shown in Figure 3. The peak at high wave number ($\sim 2000\text{ cm}^{-1}$) is unique for electrolyte oxidation and suggests that a conjugated double bond or a triple bond between carbon and oxygen could have formed. These results agree with molecular calculations performed for both radical cations of the solvents (see scheme 4). The similarities of the SEI layer between the unused and cycled cells on both anodes and cathodes indicate that SEI layer dissolution may not be the cause of cell failure in cell 117.

FUTURE RESEARCH

Although majority of the SEI layers on both electrodes appear intact and no significant changes were observed for the cell that cycled and failed, mapping the electrode surface with synchrotron beam will help to identify the homogeneity of the surface film and allows one to locate fine cracks of the surface film. Therefore we should be able to compare the SEI layers between cells from different conditions, such as abused, cycled or aged, which could link to the possible failure mechanism of the ATD batteries. Future efforts also include studying the formation process of SEI layers utilizing infrared spectroscopy.

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